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Improvements of Brazilian carbonization industry as part of the creation of a global biomass economy

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Abstract

Brazil is the largest world charcoal producer. Surface kilns with semi-spherical form built with bricks with or without recovery of by-products called "Tail Quente" are the most important systems used for charcoal production. The un-recovered pyrolysis products released to environment by this technology are major pollutants.

Some alternatives integrating existing or improved carbonization units within a global biomass economy are presented. In these alternatives the carbonization reactors can be used for primary biomass conversion, for densification, for power and heat production or as core technology in new bio-refineries. Some of the technical and economical limitations to implement these concepts are discussed.

Keywords: Wood carbonization; Charcoal; Bio-oil; Bio-refineries; Biomass economy; Brazil

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Contents

1. Introduction

Brazil is the largest world producer and consumer of bio-energy. Factors like climate diversity and abundance of forest and agricultural resources, have contributed to achieve high levels of biomass use. In 2003, 29.6% of the energy consumed in Brazil was from biomass [1]. The production and uses of ethanol and charcoal are perhaps the best-known examples of Brazilian success in bio-energy.

Most of the charcoal produced in Brazil is used in the iron and steel industry. Brazil is one of the largest producers of fused iron, steel and iron based products with 239 million tons exported during year 2005 [2], generating 242,000 direct employs and more than 1 million of indirect employs [3].

Although Brazil is the largest consumer and producer of charcoal [4,5], methods for charcoal production are still, basically, traditional processes that have very low recovery of derivatives with a very negative environmental and social impact [4–15]. Powerful green house gases like methane are released during charcoal production.

Used carbonization technologies have very low efficiency measured in terms of charcoal yield. In 2004 were used 39.7 Mt of wood, from which only 10.09 Mt were converted into charcoal [1]. It means that the conversion was approximately 25 mass%. The wood used for carbonization comes from native forests [14] or, in its majority, from reforested eucalyptus plantations [16]. In 2000, 2.97 million hectares of eucalyptus were cultivated in Brazil [3], 51.6% of which was produced in the State of Minas Gerais [17].

Reduced growth of reforested areas compared with the rate at which the demand increases as well as the increase in the distances between charcoal production and final consumers are the main causes for an existing perception of lack of wood, popularly known as "forest shortage". Some iron and steel producers are looking for alternatives to a potential charcoal "shortage" [16]. This explains the slight—and evident—growth in the import of metallurgic coal and coke. In 2000, 13 Mt of metallurgic coal were imported; in 2004 this grew to 14 Mt, 70% of which were transformed into coke [1]. The coke imported grew from 1.6 Mt in 2000 to 2.05 Mt in 2004 [1]. The amount of charcoal produced grew in the same period to a larger rate (see Fig. 2).

The development of a controlled, flexible, multi-products and integrated carbonization industry is a pressing need [18]. The improvement of carbonization industry could be framed into a more ambitious strategy for the creation of a global biomass economy. A global biomass economy requires the development of units for the initial biomass conversion near to biomass resources, centers of densification and larger centralized conversion units or bio-refineries allowing the production of electricity, bio-fuels, fertilizers and chemicals at costs competitive with the ones obtained by the petroleum economy.

The objective of this paper is to explore some alternatives to improve the Brazilian carbonization industry in the context of the creation of a global biomass economy. The alternatives presented are based on the present charcoal needs and the potential advantage of other products derived from biomass carbonization.

2. Charcoal production (products and uses)

2.1. Current situation

Charcoal is produced by a thermo-chemical process called slow pyrolysis or "dry distillation" [5,6]. A solid residue with higher fixed carbon results from the cracking of biomass weakest oxygenated bonds. Charcoal, pyrolysis vapors and gases are the main products. A liquid composed of two phases known as decanted oil (or tars) and pyroligneous acid can be obtained after condensing the vapors.

Several physical and chemical steps occur during the carbonization process. The first step is the drying of the raw material at temperatures up to 170 °C [5,6]. The initial volatiles are formed between 170 and 270 °C. These volatiles are mainly composed of CO, CO_2, methanol and acetic acid. These compounds are mainly formed from the hemicellulose and lignin. The process became self-sustainable after 270 °C, temperature at which the exothermic reactions predominate. Heating to 500 °C leads to the production of a charcoal with acarbon content of approximately 84 mass% [5,6,19]. This charcoal is similar to the coke [19], but with lower ash content.

2.2. Brazilian carbonization kilns

The carbonization kilns used in Brazil are of three types [5,6,15]:

- internal heating by controlled combustion of the raw material,
- external heating by combustion of firewood, fuel oil or natural gas; and,
- heating with re-circulated gas (retort or gas converter).

The internal heating kilns: start their operation with the controlled introduction of air to burn part of the biomass to heat up the kiln. Up to 20 mass% of the wood is sacrificed to generate the energy to maintain the process. Around 60 mass% of the wood is converted to gases and vapors [5,6]. This is the oldest method to produce charcoal [6,20]. The used kilns are manually loaded and unloaded. Examples of these kilns are: the earth kilns (no longer used in Brazil), the kilns of "alvenaria" and metallic kilns [4,5,10,15]. In the group of alvenaria kilns are the kilns of "encosta" and the kilns of surface. More than 70% of the charcoal produced in Brazil is produced in kilns of "Alvenaria" of surface of the type "Quente Tail" [4,6].

The kiln Quente Tail, is semi-spherical, built with cooked bricks and joined with mud. It has an access door for loading and unloading, without chimney. The average diameter of the base is approximately 3 m and its height 2.3 m [6]. The air enters the kiln by eight distributed holes at the base. Gases exit through 21 distributed holes in its entire surface. The process is controlled by progressively closing the air inlet holes. The smoke color indicates the progress of the operation [5,6]. The complete cycle of carbonization goes from 5 to 7 days, where 3 days are for charcoal cooling [10]. Its efficiency, measured by the yield of charcoal is commonly between 22 and 27 mass% [5,6].

The external heating kilns: have an external combustion chamber to burn some type of fuel (charcoal fines, biomass wastes, natural gas, etc.). The hot combustion gases are used for the charcoal production. These kilns allow a better control of the process and the obtained charcoal is of better quality; nevertheless, they are more expensive to operate and have higher installation costs. These kilns are mostly used in large iron and steel plants.

The kilns type retorts: are heated by the recirculation of gases. They are continuous and use a heat outsourcing to heat the biomass. An important difference of these kilns with the previous ones is that here the recovery of gases is possible. The charcoal produced is of better quality, larger yields are obtained but with higher installation costs. The use of this type of kilns is only justified with the use of co-products in the so-called carbo-chemistry. The only existing kiln of retort reported in Brazil, belongs to Acesita Company [6].

2.3. Other carbonization kilns (pyrolysis reactors)

Pyrolysis of biomass went through a technical renaissance in the 1970s thanks to new concepts and processes targeting an increase in the yield of liquid fractions. Aggressive research programs directed toward the application of newly created or improved technologies like fluidization, ablative and vacuum to design new pyrolysis reactors were undertaken. Achievements in the understanding of pyrolysis phenomena together with extensive scale-up helped to develop new pyrolysis companies (e.g., Ensyn Technologies, Dynamotive, BTG, Fortum, Pyrovac, Bioware). These companies use fluid and transport bed, circulating fluidized beds (CFB), rotating cone, ablative and vacuum pyrolysis reactors. An exhaustive review of the state-of-the-art for different pyrolysis technologies has been published by Meier et al. [21] and Bridgwater et al. [22,23]. All these reactors were designed to convert granular or dusty materials and cannot be used for logged biomass. Very few research and development has been carried out in the last 100 years to improve pyrolysis reactors using large biomass pieces like the ones resulting from eucalyptus plantations.

Perhaps the best carbonization reactors adapted to operate with logged biomass were the ones used by the old wood distillation industry still active until the beginning of the

20th century [20]. Sophisticated batch and semi-continuous reactors like American, Schwartz, Ljungberg, Ottelinska, Reinchenbach, Leschhorn, Swedich, Bosnian Meiler and Meyer kilns were operated at industrial scale. Reichenbach designed the first kiln in which the heat required for initiating and carrying out the process of carbonization was transmitted through metal walls. The choice offered in regard to the carbonizing apparatus design was not a small one. Some continuous industrial reactors were developed at the beginning of the twentieth century. The wood was charged and removed continuously, all operations being practicable without any interruption. The Gröndal retort is an example of this kind of equipment [20].

The carbonization of powdery biomass in large reactors designed to operate with larger pieces offered important technical problems due to the creation of an insolating layer of charcoal in the neighborhood of the heated surface hindering further penetration of heat. A larger number of reactors designed to operate with logged or waste biomass are needed for a diversified and sustainable carbonization industry integrated in a global biomass economy.

2.4. Charcoal uses in Brazil

The charcoal produced in Brazil is mainly used as fuel in the industry of iron processing and steel production, as shown in Fig. 1 [1].

Fig. 2 shows an increase in the charcoal production and demand in the industry of processing of iron and steel during the last years.

The main advantage of the charcoal compared to the mineral coal is that the former does not contain lead, sulfur or mercury and has lower ash content. All this makes the charcoal the best option in the process of iron reduction. Nevertheless, the charcoal has many other uses poorly explored in Brazil, for example, in sugar refinement, as absorbent, in the agriculture as soil amendment, etc [24–26]. Charcoal is an excellent feedstock for gasification. It can be gasified in conventional single step gasifiers to produce a synthesis gas with very low tar content.

2.5. Other products of the carbonization and their uses

Un-condensable gases and vapors are also formed during the carbonization process. These sub-products are still poorly used in Brazil. Condensable liquids could represent up

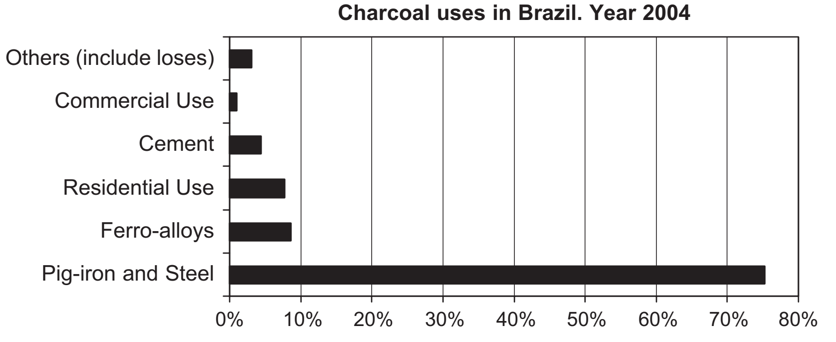

Fig. 1. Charcoal uses in Brazil during year 2004 [1].

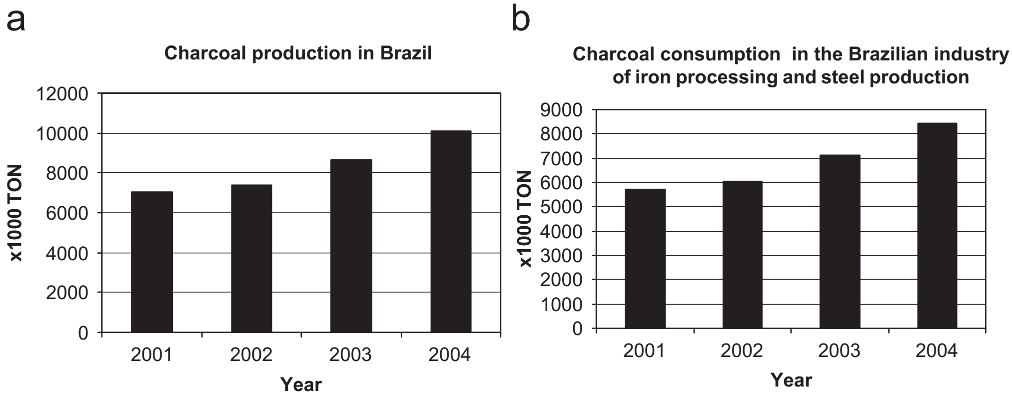

Fig. 2. (a) Charcoal production in Brazil and (b) charcoal consumption in the iron and steel industry in Brazil [1].

to 42 mass% of the initial biomass. The total condensation of pyrolysis vapors leads to the formation of a liquid made up of two phases: pyroligneous acid and decanted oil. Water is the main component of pyroligneous acid. In addition to water, several other chemical compounds exist, for example: acetic acid, sugars, methanol, acetone, etc. Their recovery in the XIX century was made at industrial scale [20], with results that today could surprise. The partial condensation at temperatures higher than 60 °C leads to the formation of an oily material commonly known as whole pyrolysis oil. Pyroligneous acid with very low contents of tar materials is obtained with the further condensation of lighter fractions.

Biocarbo (http://www.biocarbo.com) in association with Vallourec & Mannesmann Tubes (V&M) is the only Brazilian company commercializing products from decanted tars [25]. Up to 30 mass% of the tar is used by the Biocarbo to produce glues and a sealing material, the rest is used to generate energy within the V&M [25].

Important progresses have been made in the last 20 years in the development of new products from pyrolysis liquids [27]. Today it is possible to visualize new concepts of bio-refineries from pyrolysis liquids. Fig. 3 shows some of proved alternatives to obtain products from pyrolytic oils.

3. Ideal of a global biomass economy

According to Faaij [28], six stages are necessary for the implementation of a global biomass economy. The first stage consists on the use of residuals in the place where they are generated (for example, municipal residuals, residual of the paper industry, residual of the sugar-cane industry). The resources are available and generally have a negative value. Using these wastes contribute to solve at the same time a pollution problem. The production of charcoal from other residual organic solids could be an interesting option for Brazil. Reactors adapted to carbonize the very diverse residues must be available.

The second stage corresponds to the use of biomass by-products resulting from the forest and agriculture activities. These resources are more expensive to collect and to transport than the wastes but they are still profitable. The main limitation is that this stage requires the construction of a new infrastructure. Brazil has also great potentials

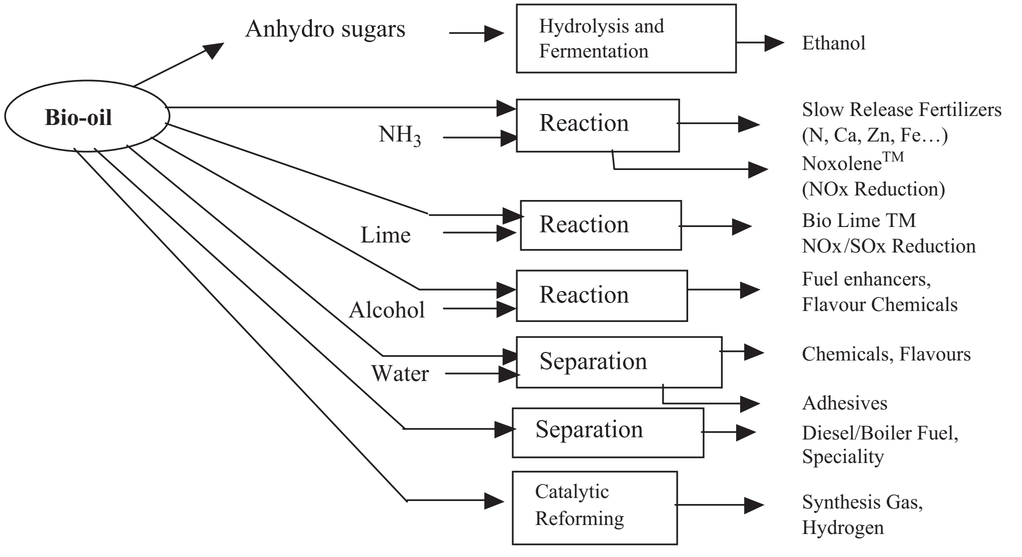

Fig. 3. Bio-oil conversion products [27].

using sub-products from the sugarcane industry or from other forest activities in the production of charcoal.

The third stage corresponds to the development of a regional biomass market, with larger and flexible conversion units. An increase in the transport cost must be expected as a result of the increase in the distances. However, economic improvements due to the use of the economy of scale must help to the viability of these units. Important political measures are needed to arrive to this stage.

The fourth stage consists in the development of a national market with an increase in the number of providers and buyers. Bio-refineries are a key component at this stage, more complex logistics is needed.

The fifth stage is associated with an increase in the size of the markets and in the distances at which the products are transported. An increase in the transport of bio-products throughout the borders is expected.

The last stage could be characterized by a natural and fast process of growth in plantations, technologies and business associated with the biomass economy. This means increase in the number of people dedicated to the production, conversion and commercialization of biomass.

The improvement of the Brazilian carbonization industry can be carried out as a part of a wider vision in parallel to the emergence of a global biomass economy. A global biomass economy requires the existence of multiple technologies, at all the scales, allowing the integral and economic conversion of all biomass resources. New technologies for biomass primary conversion for densification and for bio-refineries must be developed. The main goal is to obtain energy, chemicals, fertilizers, food, fuels and other products substituting the ones presently produced from petroleum. A global biomass economy will require the development of technologies to exploit very diverse biomass resources to satisfy local and global markets (see Fig. 4).

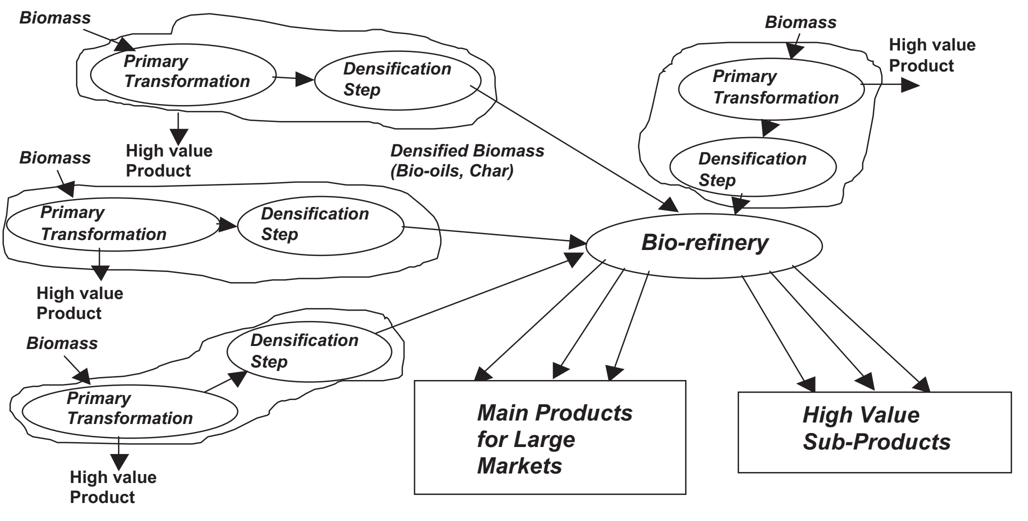

Fig. 4. Scheme of a centralized bio-refinery operation, with satellite units for primary transformation and densification units [29].

Primary conversion units oriented to obtain products of high commercial value must be located near to the biomass resources. Sugar cane and pulp and paper industries can be considered as primary conversion units. The carbonization plants existing in Brazil can be framed in this category because their main goal is to produce a single product (charcoal) near the biomass resources. The densification unit is needed "to concentrate" the energy contained in the biomass allowing its transport to distant bio-refineries. Several technologies can be considered for densification. Mechanical processes, like production of pellets, thermal processes, like torrefaction [19,30] and pyrolysis can be considered as densification strategies. The development of biomass densification technologies is an important element in the creation of a global biomass economy.

The bio-refineries are large units operating with raw biomass or with wastes from the primary conversion units and their goal are to use the economy of scale to produce several products. Many new concepts based on chemical, thermal, mechanical and biological based conversion technologies are under-development worldwide to offer in the near future a critical mass of options that could catalyze the emergence of a global biomass economy [31–37].

In the next section are presented different alternatives in which pyrolysis or carbonization units are located as: (1) part of the primary conversion or densification units, (2) part of the bio-refineries. The success of these technologies will depend on the way their development is synchronized with the different stages previously described for the formation of a global biomass economy.

3.1. Use of carbonization units as part of primary conversion or densification units

3.1.1. Alternative 1: charcoal production and combustion of pyrolytic vapors in situ

This alternative raises the possibility of producing charcoal as primary product in plants that operate with pyrolysis reactors coupled with boilers. The combustion of gases and

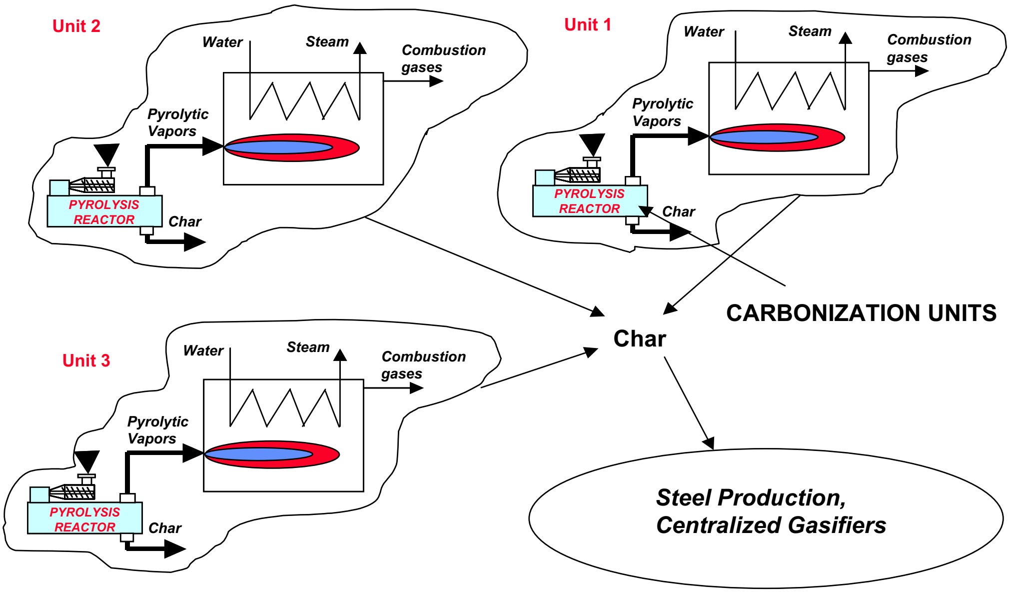

Fig. 5. Integration of charcoal production units with gasification units.

pyrolysis vapors could be carried out with heat recovery to produce steam to generate electricity in steam turbines.

The coupling of pyrolysis reactors with boilers is a very promising alternative because it allows the use of biomass as a fuel in boilers designed to operate with natural gas or other liquid fuels without any major modification in the combustion chamber. A similar co-combustion concept but using gasifiers has been demonstrated with the successful tests of co-combustion schemes in Lahti (Finland) and in Amer (Holland) [38]. A scheme of this alternative [39] is presented in Fig. 5.

The charcoal produced in this concept could be transported towards consumption centers, to produce iron and steel and/or to centralized gasification units to produce synthesis gas. The great advantage of gasifying charcoal is that the produced gases will have very low content of tar, making it a very attractive option for using gas turbines and diesel engines designed to operate with clean gases [40]. Synthesis gases with low content of tar can be used to produce transportation fuels throughout Fischer-Tropsh. The diversification of charcoal industrial uses is necessary to reduce the dependence to the iron and steel industry. The coupling of pyrolysis reactors with boilers is an area very poorly studied in the literature. This alternative could be used in small and medium size units like the used ones presently in Brazil to produce charcoal.

3.1.2. Alternative 2: production of charcoal and bio-oil. Use of bio-oils as fuels in advanced cycles

Alternative 2 is similar to alternative 1 but the pyrolytic vapors are condensed and the obtained oils used in advanced cycles like for example integrated gasification combined cycles (IGCC), in gas turbines or in diesel engines. The integration of pyrolysis units with these advanced cycles is known as integrated pyrolysis combines cycles (IPCC) [41]. The

bio-oil is transported from units located near to the biomass resources to larger central power plants.

The bio-oils can be gasified in high-pressure gasifiers. A very interesting process for the gasification of bio-oil in charcoal slurries is under study in Germany [42]. The produced syngas can be directly used gas turbines or to generate transport fuels throughout Fisher-Tropch (Fig. 6). The IPCC has efficiency larger than that one of a Rankine cycle [41]. This kind of system does not require the use of gas compressors and the difficulty is reduced to join the biomass processing units with the systems of power generation. Leader companies in the production of high-pressure gasifiers are Foster-Wheeler (USA) [43] and Carbona Technology (Finland) [44,45].

The direct use of bio-oil in gas turbines, as tested by Teledyne CAE (USA), Orenda Aerospace Corporation (Canada), University of Rostock (Germany) [39], etc., is another interesting alternative, but this scheme requires of the use of a compressor for the operation, aspect that influences in the reduction of the cycle efficiency.

The only system on commercial scale producing heat from bio-oils operates in the plant of Red Arrow Products, Wisconsin [39], with capacity of 5 MWth. The emissions of CO, NO*x* and formaldehyds are under the allowed levels of emissions. All these results confirm the viability of replacing heavy fuel oils per bio-oils [35].

The use of the bio-oil to operate diesel engines and to generate electricity has been evaluated elsewhere [39], with promising results. The diesel engines offer high efficiency (over 45%) in the power generation and can easily be adapted in combined cycles for generation of heat and power (combined heat and power process, CHP) [39]. The use of crude pyrolysis oils as fuels have been extensively studied in the literature, however, many technical problems remain unsolved [46]. Some of these problems are described in the following section.

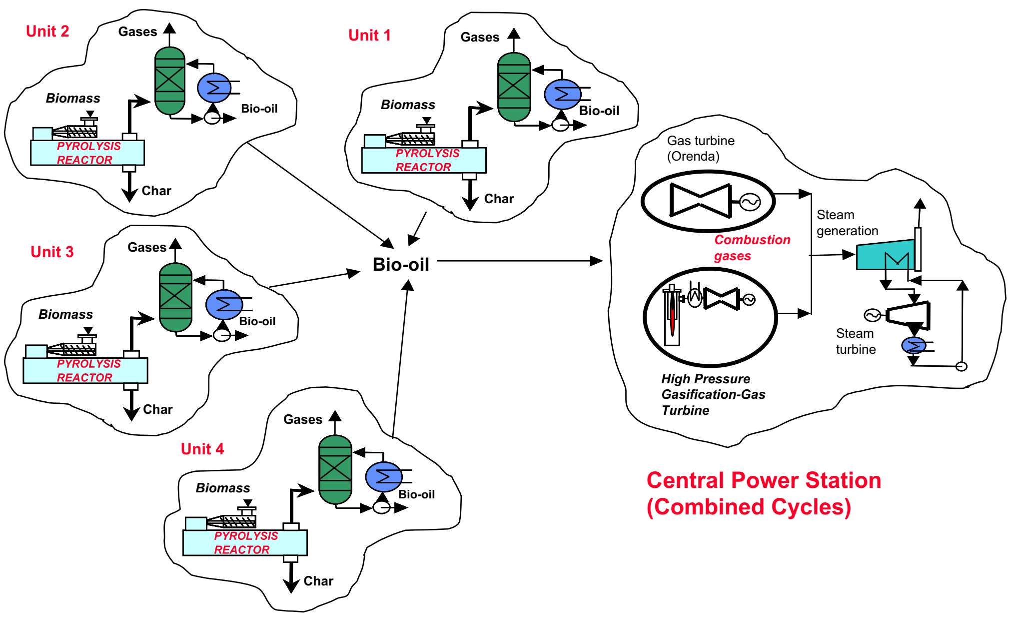

Fig. 6. Integration of charcoal production with the generation of electrical energy in combined cycles.

Use of bio-oils as fuels in advanced combustion systems.

Some of the most common reported problems in the use of bio-oils as fuels are:

(1) Change in chemical and physical properties (e.g. increase in viscosity) during storage. This phenomenon is usually known as "aging" and is caused by the occurrence of many chemical reactions in the storage tanks [47–51]. From a practical point of view, a minimum of 14 days of storage should be possible; preferably the bio-oil should have at least 6 months of storage life (at normal pressure and temperature of 25 °C) [52,53].

(2) The complex multiphase properties of bio-oils [47,52,54–56] can create serious problems during storage and handling [57]. The layering or separation of bio-oil phases can be a problem in installations that do not have facilities to homogenize these liquids [52,55,56–58]. Specifications must ensure that bio-oils are supplied as homogeneous liquids. Some storage tanks (specially the ones for daily supply) should include pumps for recirculation and/or stirrers to prevent phase separation [51,52]. The use of additives (like ethanol, methanol or higher alcohols) can help homogenize bio-oils [49,55,59].

(3) Bio-oils have a distinct acrid smoky smell, which can irritate the eyes if exposed for prolonged period of time [23]. To handle this problem, the storage tanks need to be closed and the immediate local environment must be adequately ventilated [52,60].

(4) If the construction materials for the tanks are not properly chosen, important corrosion problems may occur. The corrosive character of bio-oils is mainly due to the presence of acetic and formic acids that contribute to pH values around 2.2 [50,61]. It has been recommended that tanks, fuel lines, pumps, heaters and nozzles must be made of 316 stainless steel (SS), copper or various plastics like polyester resin and poly-olefins [41,50].

(5) The use of on-line filters is highly recommended to avoid nozzle plugging and erosion by fine particles [51,62]. The maximum allowable content of char and its particle size distribution in the commercialized oils will have to be guaranteed by the suppliers [51,52]. Bio-oil filtration and atomization must be carried out at temperatures higher than 60 °C [57].

(6) Re-start problems after periodic operation of combustion systems using bio-oils are a commonly observed phenomenon. Often, the feeding system is totally clogged after 24 h of interruption [63]. This clogging can be due to bio-oil accelerated thermal polymerization, due to the re-crystallization of waxy materials [57]. The nozzles and feeding lines must be flushed, cleaned and cooled after each operation [50]. The feeding system must be conveniently modified to allow on-line switching for cleaning and pre-heating [64]. The operation off/on must be limited [50].

(7) The use of bio-oils can produce nozzle erosion (resulting in enlargement of the injection channels), abrasive wear of fuel pumps and attrition and erosion of other moving parts [22,64–66]. All these phenomena generate rapid decrease in performance and prevent long-term operation.

(8) Bio-oils have very poor lubrication. Lubrication is critical in diesel engines because the fuel itself lubricates vital parts of the injection system. Some additives can be used to improve bio-oil lubrication properties [64].

(9) High tendency to form solid residues in the nozzles. The use of nozzle cooling devices is recommended: "for example a core air channel surrounding the bio-oil lance and atomizer or any other anti-coke formation devices" [52]. The atomizers must be designed with minimum internal complexity [52].
(10) Bio-oil sprays pulsation arising from the formation of vapors inside the nozzles. These vapors can be formed by overheating the bio-oil in low feeding pressure systems (feeding pressure lower than 50 bar). Bio-oils contain very volatile compounds in comparison with the defined fraction of gasoil. This problem can be reduced by controlling the water content and other volatile fractions in the bio-oil. It can also be alleviated with strong swirl [51,59].
(11) Larger vaporization and combustion times requiring bigger combustion chambers [67–70].
(12) One of the main problems found with bio-oils is the ignition difficulty in "cold" environment. Spark ignition is not normally successful. This problem is mostly associated with the low content of light organics and the high water content in bio-oils. It can be overcome by preheating the combustion chamber before introducing the bio-oil [50,51,59,71–75].

3.2. Use of the pyrolysis reactors as part of bio-refineries

The bio-refinery is a system integrating several processes of biomass conversion having the necessary infrastructure to produce fuels, chemical products and energy from biomass. This concept is similar to the one of a modern petroleum refinery, but modified to accept different types of biomass. Bio-refinery results from the bridge between agriculture, chemistry and engineering [35].

Although the idea of bio-refineries is not new, the recognition of its strategic and economic potential is recent [76]. Before first half of the last century, important industrial movements exposed that anything that is elaborated from hydrocarbons can also be elaborated using lignocellulosics [77]. The present conception of bio-refineries will not eliminate the necessity of chemicals derived from petroleum but it is expected that they are going to reduce the petroleum dependency contributing to a more sustainable XXI Century [78].

The bio-refinery concepts presented in this section are, in general more complex than ones presented in the preceding section requiring a greater technological level than only can be achieved at relatively large scales.

All viable bio-refinery concepts require some kind of densification units located near the biomass resources from where the densified material is supplied to centralized units. Existing carbonization units with condensation of pyrolysis vapors considered can have a function in the biomass economy similar to the one petroleum wells have in the petroleum economy.

In this regard, some existing carbonization units could play a function as densification units. Other alternatives could be: wood torrefaction, or the production of pellets. The kilns presently used for carbonization are not adapted for torrefaction, for this reason it is necessary to develop and to build new kilns and new densification technologies. New processes like the one proposed by Transnational Technology [79] are a good example of these kinds of new densification processes.

All the alternatives described in the following section are based on the use of densification units as primary element in the operation of bio-refineries.

3.2.1. Alternative 1: separation of bio-oil in bio-refineries to obtain fractions

Most of the studies so far conducted use crude bio-oils to produce final products [27,76] (see Fig. 2). Products of better quality, with better performance and reproducibility could be obtained if the bio-oils were refined and separated in fractions. Several strategies for bio-oil separation have been reported in the literature [80,81]. These strategies are based on solvent extraction or in distillation to achieve the desired separation. The existing solvent separation methods are based on the differences of polarity or acidity as the driving force for the separation. An excellent review of the different schemes of separation has been presented by Fagernas [80], and Oasmaa et al. [81]. Any of these strategies could lead to a new concept for bio-refinery. The scheme presented in Figs. 7 and 8 is only one of these possible alternatives.

The technology presented in Fig. 8 is based on the hypothesis that the maximum amounts of distilled products, the products of greater value, will be obtained if:

(1) Oligomeric compounds and chars present in pyrolysis vapors are removed before condensing the bio-oils. The content of char in bio-oils is presently determined by the efficiency of cyclones, which remove particles 410 μm. The solids left may be removed by on-line hot-vapor filtration, or centrifugation/filtration of condensed pyrolysis liquid. The separation of char particles in the hot gases could be also performed based on the principle of the rotational particle separator (RPS) (US-patent US5073177) as proposed by the University of Twente.
(2) Bio-oil condensation systems are designed to reduce the polymerization of bio-oils in this way reducing the content of oligomers in condensed oils. This can be achieved using hot-condensers with in-miscible or partially miscible auxiliary liquid. The temperature

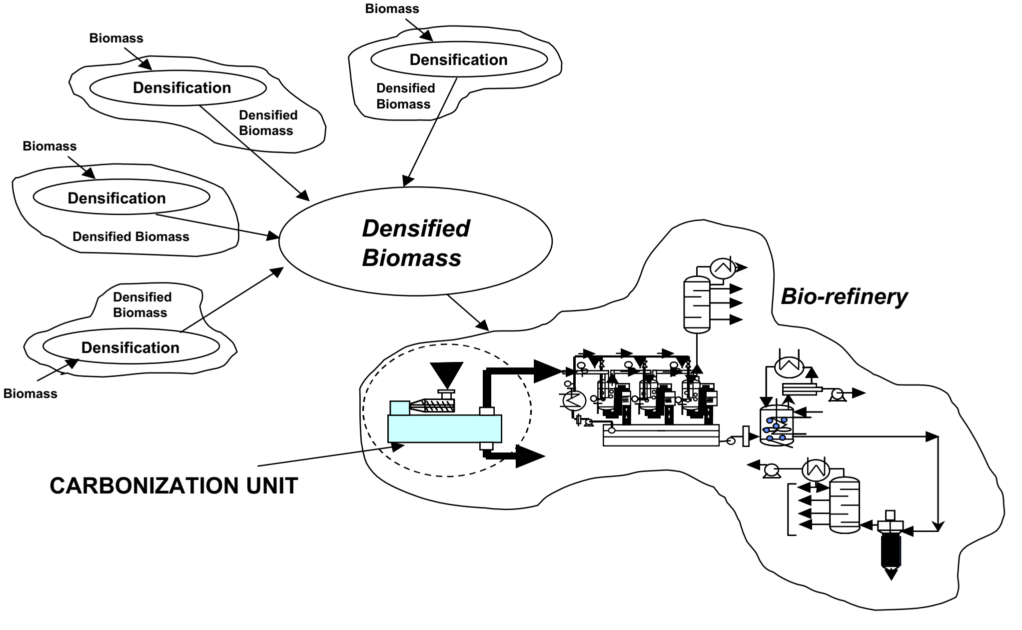

Fig. 7. Integration of densification units with a centralized bio-refinery.

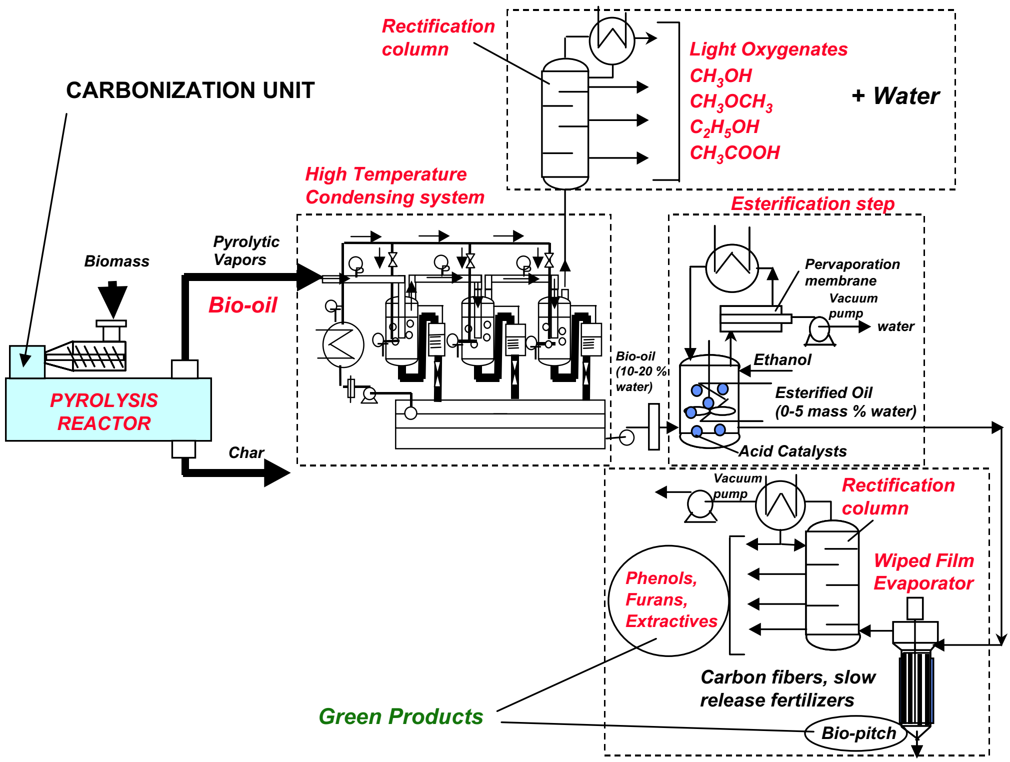

Fig. 8. Tentative concept for a bio-oil base refinery.

of liquid scrubbers is increased to distil off the lightest reactive aldehydes and ketones with some water and acids (loss of organics below 10 mass%).

(3) The bio-oil is stabilized immediately after condensed. The stabilization of the oil could be carried out through a process of esterification with ethanol or methanol. Addition of alcohol improves the homogeneity and storage stability of the liquid and decreases its viscosity. Addition of alcohol is beneficial also in solids removal. It dilutes the liquid, reducing its stickness thus enhancing the filterability of the liquid.

(4) The water present in bio-oil limits the esterification equilibrium and as so it must be removed from the esterified oil if it is desired that the process of esterification arrives at high levels of conversion. New process to remove water from bio-oils need to be developed.

(5) The distillation of oils is carried out as fast as possible to reduce the impact of poly-condensation reactions leading the formation of bio-pitches. The molecular distillation could be a useful tool to achieve a fast distillation.

The technology presented in Fig. 8 proposes the pyrolysis of the biomass in a central refinery and the separation of pyrolysis vapors to obtain: methanol, ethanol, acetic acid, acetone, phenols, furans, bio-pitch. New fuels must be obtained from the distilled fractions. The economic viability of this alternative will depend on the capacity to develop

new competitive products for the obtained fractions. Several new products like polyurethane elastomers and bio-carbon electrodes, have been developed from the bio-pitches [82–87]. Part of the technologies needed to achieve this step already exist, however, a serious integration effort is needed to prove the viability of this or others bio-refinery concepts.

3.2.2. Alternative 2: production of carbonaceous materials and hydrogen

In this alternative, the pyrolysis of biomass is followed by a high temperature poly-condensation of pyrolysis vapors to produce soot and gases rich in CO_2, CO, methane and hydrogen. Soot or carbon black is the generic name for an elementary form of carbon produced of the vapor phase of the pyrolysis by combustion of a hydrocarbon in a limited air atmosphere. One of the problems existing in the Carbon Black production is that it is excessively polluting [88], this because the used raw material is mineral coal. This situation can be reverted when using biomass with ecologically viable processes, like the proposed one.

Around 90% of the carbon black produced from natural gas is used in the rubber products production—where the tires are predominant—or like pigment for rubbers, inks, paintings, etc. Very few studies have been carried out to find new applications of biomass-derived carbon black.

The technology presented in Fig. 9 is based on the idea that if the pyrolysis vapors are heated to temperatures up to 1200 °C in a reducing atmosphere, great part of these vapors is going to be turned to soot, water and syngas [89].

Morf et al. [89] reports that if the pyrolysis vapors are heated to 1000 °C in the absence of oxygen then a syngas rich in CO_2 (13 mass% of dry biomass), CO (7 mass% of dry biomass), CH_4 (2,3 mass% of dry biomass) and hydrogen (0.4 mass% of dry biomass) will be produced. The pyrolysis vapors will be mostly converted to soot yielding 23 mass% of dry biomass. This high yield of soot suggests the economic viability of this alternative. New products from biomass soot must be developed.

The syngas can be reformed to produce more hydrogen. Hydrogen is being accepted as a future alternative fuel for automotive use [90], and the integration of processes based on the biomass, as the proposed one, could have an important participation for obtaining it.

3.2.3. Alternative 3: production of charcoal and/or synthetic gas by means of biomass gasification

The production of synthesis gases from biomass must be considered as a way to diversify the Brazilian eucalyptus biomass industry. The production of transportation fuels from syngas is an alternative to the use of charcoal in the iron and steel industry. Existing carbonization units could be optimized to produce solids or synthesis gases depending of their location and demand of products.

Syngas is the name granted to gases generated in the process of gasification of mineral coal, biomass, natural gas or other organic remainders. It consists mainly of CO and hydrogen. Transportation fuels can be produced from syngas using the Fischer-Tropsch synthesis (Fig. 10).

The range of products immediately obtainable from syngas extends from bulk chemicals like ammonia and methanol, through industrial gases to utilities such as clean fuel gas and electricity. For most syngas derived products, syngas production accounts for between

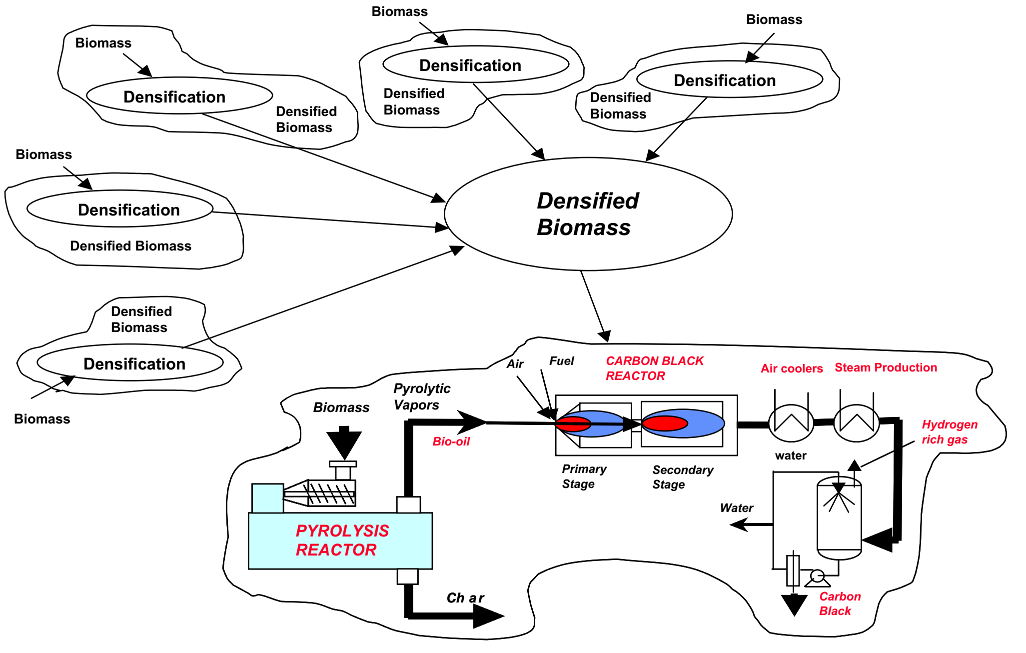

Fig. 9. Production of charcoal, carbon black and hydrogen.

50% and 75% of the product cost [91]. Some of the catalytic pathways to convert syngas are presented in Fig. 11.

Syngas conversion technologies to obtain mixed alcohols, NH_3, aldehydes, ethanol, waxes, diesel, olefins, formaldehyde, MTBE, DME has been extensively documented in the literature [91].

The major problem for syngas production in one-stage gasifiers is the presence of important amounts of tar which requires the implementation of an expensive process of syngas cleaning, before they can be used for the production of different products as indicated in Fig. 11.

The development of two-stage gasifiers seems to have solved the problem of production of synthesis gas with high contents of tar. The processes proposed by the Choren Company of Germany [92] and by the Technical University of Denmark are examples of this type of gasifiers. Two-stage gasifiers are formed by a pyrolysis or carbonization reactor followed of a high temperature step at more than 1200 °C to convert the pyrolysis vapors into soot. The soot and the charcoal are further converted into syngas in the presence of an oxidation agent.

3.2.3.1. Option 1: two-stage gasification (Choren Process). In the Choren Process (Carvo-V® gasifier) (Fig. 12) a previously crushed and dried biomass is initially pyrolysed at temperatures between 400 and 500 °C producing volatiles and charcoal. The volatiles are further heated to over 1400 °C. In these conditions most of the volatiles are converted to soot. The charcoal and the soot (carbon black) are further gasified in a fluidized bed to obtain a synthesis gas with a very low content of tar.

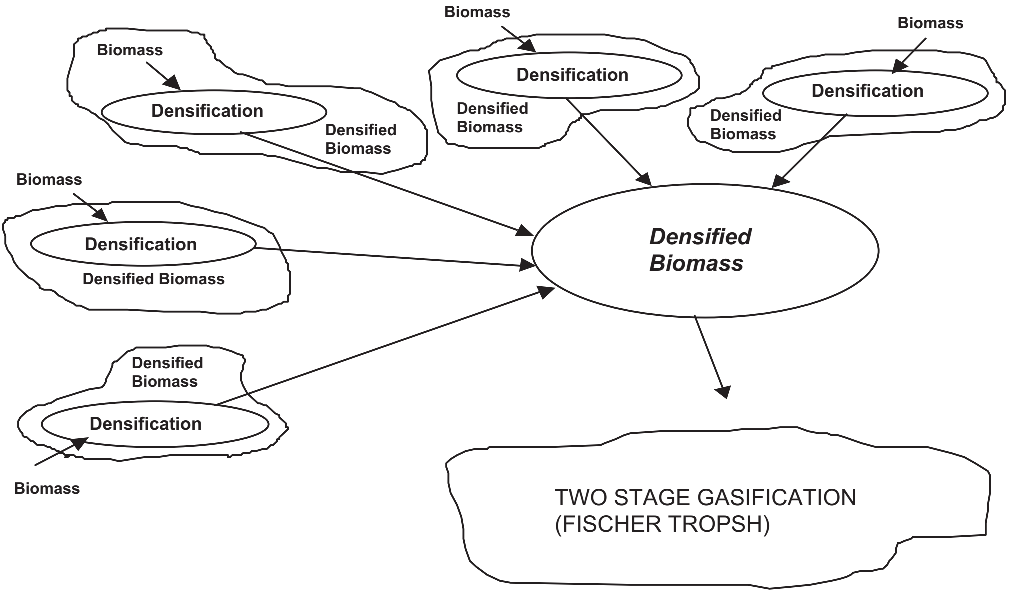

Fig. 10. Biomass gasification in two stages gasifiers.

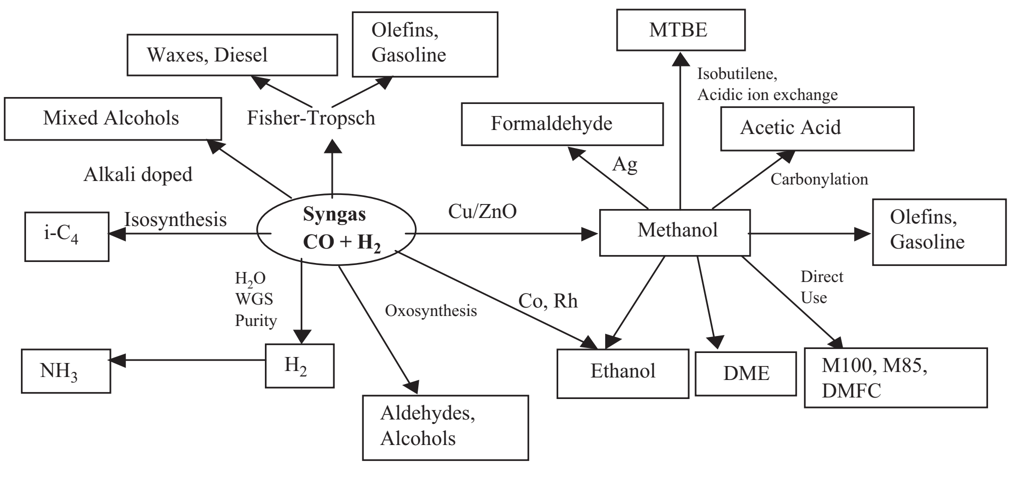

Fig. 11. Syngas conversion products [91].

3.2.3.2. Option 2: two-stage gasification (Process Technical University of Denmark). The process developed by the University of Denmark [93] (Fig. 13) is based on a concept similar to the Choren Process; the difference is that the pyrolysis vapors and the charcoal are both subjected to the high temperature step. The gasification of the charcoal and the soot is carried out in a pile not in fluidized bed as in the case of the Choren process.

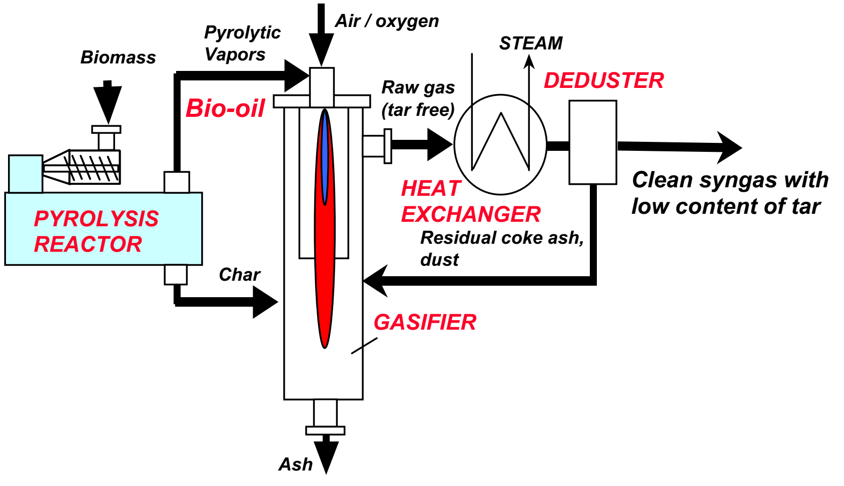

Fig. 12. The Choren process [92].

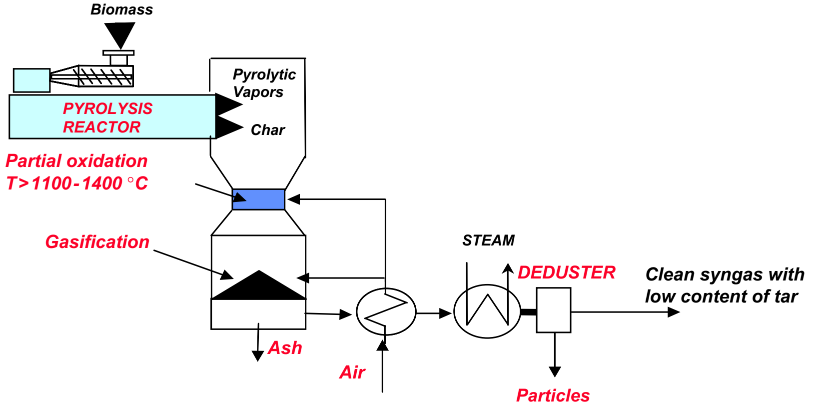

Fig. 13. Process Technical Univeristy of Denmark [93].

3.2.4. *Alternative 4: hydrogen production from direct reforming of pyrolysis vapors*

The gasification of mineral coal is the oldest method for hydrogen production [88] and it is still widely used in the world. Hydrogen could be also obtained from the reforming of pyrolysis vapors using a process similar to the one developed by NREL and commercialized by Eprida Technology [24]. Charcoal and hydrogen are two main products from this process [24].

4. Hurtles in the construction of a global biomass economy in Brazil

The implantation of some of the alternatives described to improve the Brazilian charcoal industry finds several technical, economical and social hurtles. The first and main limitation is of technical nature. Most of the technologies described for the primary conversion of biomass, for densification and for bio-refineries are not available today. New

Table 1
List of some companies that at the moment operate in Brazil in the construction of equipment that could comprise of systems based on the biomass

Company	Products	Contact
Biochamm Caldeiras e Equipamentos Industriais Ltda	Boilers for sawdust and for wood wastes	www.biochamm.com.br
Planalto Industria e Comercio Ltda	Horsebreakers of forests, descascadores, esteiras	www.planaltopicadores.com.br
Leogap Industria e Comerico de Maquinas Ltda	Wood driers	www.leogap.com.br
Benecke Irmãos & Cia. Ltda	Drying, boilers, systems of feeding, steam engines	www.benecke.com.br
SML	Wood driers	www.sml.pt
Aalborg	Wood boilers	www.aalborg-industries.com.br
Biomax	Briquetting press	
Termoquip	Gasifiers, pyrolysis reactors, dryers	http://www.termoquip.com.br/

pyrolysis reactors operating with logged and powdery biomass designed to perform well-defined function in the biomass economy are needed. Kilns for torrefaction, pelleting units, crushing machines, downstream separation units, and new biomass derived products need to be developed as part of a comprehensive approach to develop an integrated biomass industry in Brazil.

Table 1 list some Brazilian companies that could be interested in the design and construction of several of these equipments. A technological effort of this kind can be only coordinated and directed by the government or by well establish industries like the petroleum industry.

A complete list of foreign producers of gasifiers can be found elsewhere [94]. The list presented in Table 1 shows that, at least a part of the equipment needed for the implantation of systems described in this paper is available Brazil. Nevertheless, these equipments must be adapted to offer a service as part of larger technological concepts. A serious effort in process of integration is needed. The existing equipments must be adapted or new concepts developed to act in a specific context offering a service in the new biomass economy.

The second great limitation in the implantation of an economy of biomass in Brazil is the market. A new biomass economy will have to compete with the well-established procedures used in the petroleum industry. These processes tend to be cheaper due to the enormous amount of capital invested in R&D by the petroleum industry. The increase in hydrocarbon and natural gas prices could help to increase the competitively of alternatives derived from biomass.

The third economic limitation is of economic nature, since, most of the proposed concepts must be implemented at large scales to obtain economic viability. These scales require large capitals that can only be obtained with the intervention of governments and/or large companies.

5. Conclusions

The production of charcoal in Brazil is very dependant of the iron processing industry making the sustainability of this activity extremely vulnerable to changes in the market of

iron products. The alternatives presented could help to diversify this industry encouraging the production of one or another product depending on the market conditions. Some of these options can only be implemented at relatively large scales. Much research and development is still needed to prove the techno-economic viability of some of these concepts.

The development of new biomass-derived products substituting the ones presently obtained from petroleum is critical for the success of a global biomass economy.

Some social changes are expected to occur in the rural areas while introducing more efficient and integrated carbonization systems. The reduction in the manual labor required to carbonize could be used in the processes of reforestation. At the moment the states that invest more in reforestation programs are in the South and Southeast of Brazil. A greater use of reforested biomass in the states of the north (Amazonian Region) is expected to occur [14].

The presented alternatives are on line with the policy adopted by Brazil and other countries to fulfill the originating commitments of the adoption of the Protocol of Kyoto for carbon credits, due to the high degree of carbon capture by the biomass used for the described processes, when this biomass comes from reforested biomass. Brazil has the conditions to undertake more ambitious biomass programs complementing the good results so far obtained by the sugar cane industry.

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